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In planar metal-poly(*p*-phenylene vinylene) (PPV)-metal devices the experimental current is five to six orders of magnitude larger as compared to the expected space-charge limited current. Comparing these measurements with field-effect transistors demonstrates that the enhanced current originates from a high surface charge carrier density at the polymer/substrate interface. This surface charge is found to be only weakly dependent on the substrate, device geometry, and chemical treatment of the substrate. The presence of such a conducting channel due to charging of the surface obscures the intrinsic in-plane conducting properties of PPV. © *2006 American Institute of Physics*.
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I. INTRODUCTION

The light in an organic light-emitting diode (LED), typically fabricated in a sandwich configuration with the polymer layer between a hole-injecting and an electron-injecting electrode, is emitted through a transparent electrode.[1–3] This structure is suitable for display applications, but a disadvantage is the requirement of a transparent conductor as bottom or top electrode. In order to circumvent this problem Pei *et al.* used a different approach by developing an electrochemical light-emitting cell (LEC).[4] They designed a planar device with two opaque electrodes deposited on top of a substrate with a separation of a few microns. An ion-conducting luminescent polymer mixed with an ionically conductive material was spin coated on top of the device. The active layer is electrochemically *p* doped near the anode side and *n* doped near the cathode side; a *p-n* junction is formed between the doped regions. Under an applied electric field the charge carriers move toward the opposite electrode, meet within the *p-n* junction, and recombine radiatively. The main disadvantage of LECs is that their stability is very limited, possibly due to the *n*- and/or *p*-type doping of the polymer. As an alternative to LEC, surface LEDs using planar configuration with conventional light-emitting polymers have been created by several groups.[5–7] Electroluminescence from planar metal-polymer-metal structure using LED materials such as poly(*p*-phenylene vinylene)[5] (PPV) or polythiophene[6,7] derivatives has been reported. Apart from their practical applicability, these surface-emitting devices are also interesting for basic scientific studies. From spatially resolved electroluminescence measurements the emission zone in such an in-plane device can be obtained.

The transport in the plane of the polymer film is usually investigated in a field-effect geometry. In a recent study it was demonstrated that the hole transport in sandwiched hole only diodes and in-plane field-effect transistors (FETs) can be unified for heavily disordered PPV-based semiconductors.[8] The charge carrier density in a space-charge limited (SCL) diode is orders of magnitude lower as compared to the density induced in a FET. The large differences in hole mobility obtained in diodes and FETs originate from the strong dependence of the mobility on charge carrier density.[8] A direct comparison, at low carrier density, between charge transport in the plane and perpendicular to the polymer film can be obtained from the observation of an in-plane space-charge limited current (SCLC). It should be noted that such an observation is not possible in a field-effect structure with zero-gate voltage applied. Due to the relatively long distance of several microns between the in-plane electrodes large source-drain voltages are required to obtain a measurable SCLC, which will lead to a breakdown of the gate insulator. Here we study the transport of holes in planar structures using gold electrodes and PPV-based polymers spin coated on different substrates such as glass, Al_2O_3, quartz, and SiO_2. The experimentally observed in-plane current is five to six orders of magnitude larger than the expected space-charge limited current. This strong enhancement is attributed to the charging of the polymer/substrate interface. The influence of a chemical treatment of the substrate on the current-voltage measurements is discussed.

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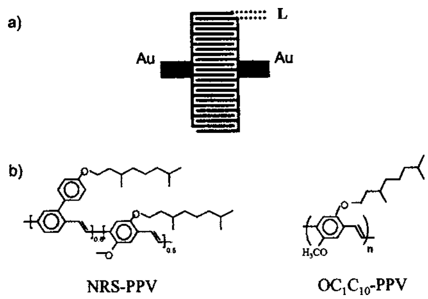

FIG. 1. Schematic representation of the planar metal-polymer-metal device structure (a). The fingers of the two electrodes are separated by a length (L) and the active channel width (W) of the device is the sum of all horizontal widths between the finger pairs. The chemical structure of the polymeric compounds (b).

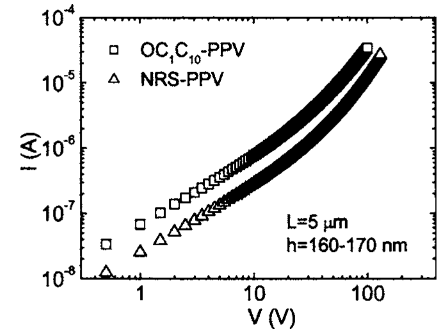

FIG. 3. Current-voltage characteristics of OC_1C_{10}-PPV and NRS-PPV in-plane diodes with polymer thickness $h=160-170$ nm and channel length $L=5$ μm.

II. EXPERIMENT

The planar device contains two gold (Au) interdigitated electrodes. A 100 nm thick Au layer was patterned onto different substrates such as SiO_2, glass, Al_2O_3, and quartz. The two electrodes were separated horizontally by a width (W) of 1 mm or 5 cm. The active channel length of the device ranged between $L=1.25$ and 20 μm [See Fig. 1(a)]. To finish the device the polymer has been spin coated over the electrodes in a nitrogen atmosphere. The thickness of the polymer varies between 80 and 600 nm and has been measured using a DekTak 6M. The two polymers used in this study are poly[{2-(4-(3′, 7′-dimethyloctyloxyphenyl))}co-{2-methoxy-5-(3′,7′-dimethyl-octyloxy)}-1,4-phenylene vinylene] (NRS-PPV) and poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vinylene) (OC_1C_{10}-PPV), and their chemical structure is presented in Fig. 1(b).

The electrical characteristics current versus voltage (*I*-*V*) of the devices were measured in different environmental conditions: air, nitrogen, and vacuum using a Keithley 1100 V SourceMeter. All voltage sweep measurements were done using small voltage steps of 0.5 V and 1 V, and a delay time for the source of 0.5 s.

III. RESULTS AND DISCUSSION

A. Materials and substrates

Figure 2 shows the experimental current (I) versus electric field (E) characteristics of Au/OC_1C_{10}-PPV/Au devices

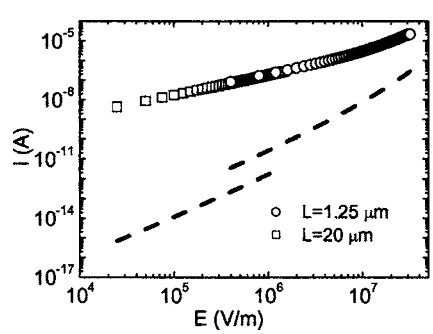

FIG. 2. Current vs electric field for Au/OC_1C_{10}-PPV/Au structure with polymer thickness 270 nm and channel lengths of 1.25 and 20 μm. The dashed lines represent the calculated current. The inset presents the in-plane device structure.

having a polymer thickness of 270 nm and channel length $L=1.25$ and 20 μm, respectively. Also included in the figure are the calculated SCL currents using the (field-dependent) mobility as determined from LEDs based on the same polymer (dashed lines) with the form $\mu(E)=\mu(E=0)\exp(\gamma\sqrt{E})$.[3] For these calculated currents the zero-field mobility $\mu(E=0)=5\times10^{-11}$ m^2/V s and the field-enhancement factor $\gamma=5\times10^{-4}$ $(V/m)^{-1/2}$ have been used. Figure 2 demonstrates that at low electric fields the current measured for a planar device is up to six orders of magnitude higher than the SCLC as expected from the LED parameters.

Furthermore, in contrast to the SCLC (dashed lines) the experimental currents scale with the applied electric field $E=V/L$. In the low-field part the experimental current scales linearly with the applied field instead of quadratic as expected from a SCLC. The strongly enhanced current cannot be due to a high in-plane mobility; in that case the current would still be quadratic and would not scale with the applied field. Another possible explanation for the large experimental current could be a strong homogeneous doping of the polymer film. In this situation, the low-field part of the experimental current would be strongly enhanced and would scale linearly with the applied field. The current is then described by $I=qp_0\mu EA$, where q is the elementary charge, p_0 the carrier charge density due to doping, μ the hole mobility, and A the area of the active channel. Using a low-field mobility of 5×10^{-11} m^2/V s the observed current requires a p_0 of 2×10^{24} m^{-3}. However, the presence of such a high background charge density is highly unlikely, since from LED measurements these PPV derivatives are known to be undoped.[3] The spin casting is performed in inert nitrogen atmosphere and the measurements are performed in vacuum ($<10^{-6}$ bar), so there is no opportunity for the samples to get doped by oxygen.

As a first test we investigate whether the observed current enhancement is specific for the OC_1C_{10}-PPV or that it also occurs for other PPV-based polymers. In Fig. 3 we present *I*-*V* measurements on both OC_1C_{10}-PPV and NRS, processed under the same conditions (substrate, solvent, environment, and device area), for a device length of 5 μm. It is observed that the current of NRS is also strongly enhanced, it is only a factor of 3 lower as compared to the OC_1C_{10}-PPV current. The hole mobility of NRS-PPV in a LED configuration has been previously determined and

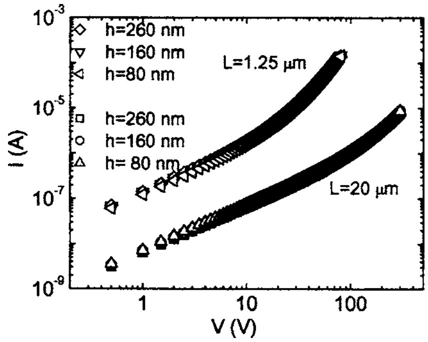

FIG. 4. Current-voltage measurements of NRS-PPV in-plane diodes as function of polymer thickness h.

amounts to 1.5×10^{-12} m^2/V s,[9] such that the difference between hole mobility for these two polymers in hole only diodes is about a factor of 30. Apparently, the effect of this mobility difference is strongly weakened in the in-plane measurements.

A simple test to check the presence of a large background charge carrier density in these polymers is to investigate the dependence of the in-plane current on the polymer thickness. For homogeneous doping the current is expected to be inversely proportional to the polymer layer thickness. For this purpose, we performed measurements for one polymer with different layer thicknesses in the device. All the devices were made from one single polymer in toluene solution using different rpm in order to obtain different polymer thicknesses. The results of this experiment are presented in Fig. 4 for NRS-PPV for $L=1.25$ and 20 μm. These measurements clearly demonstrate that the in-plane current is independent of the thickness of the polymer layer. From this observation doping of the polymer layer can be excluded as the origin of the enhanced in-plane current.

The absence of any scaling with the polymer film thickness suggests that the enhanced in-plane current mainly flows along the substrate/polymer or polymer/vacuum interface. In order to check whether the substrate influences the measurements, we used different substrates such as quartz, glass, Al_2O_3, and SiO_2, with roughness of 0.5–1 nm. In Fig. 5 measurements for NRS-PPV samples are presented for three different substrates. The measurements are scaled for the channel width and length of the devices. These measurements show that the current enhancement is not sensitive to the substrate used.

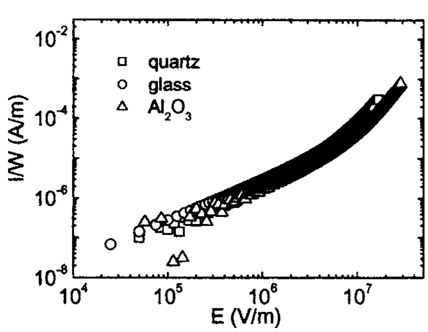

FIG. 5. Current-voltage characteristics of NRS-PPV in-plane diodes as a function of substrate (glass: $L=20$ μm, $h=160$ nm, quartz: $L=60$ μm, $h=425$ nm, and Al_2O_3: $L=27$ μm, $h=200$ nm).

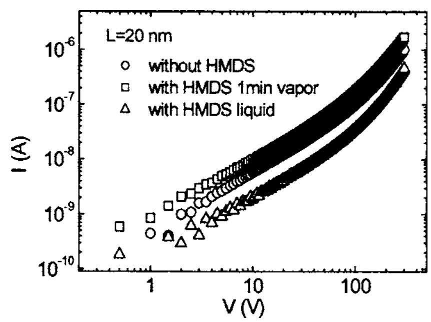

FIG. 6. NRS-PPV planar device for which the substrate surface was treated with HMDS.

B. Influence of the substrate treatment

From polymeric LEDs and FETs it is known that a treatment of the substrate surface with different solvents, oxygen plasma, ultraviolet ozone, etc., strongly influences the electrical characteristics.[10–13] For example, the SiO_2 surface of a FET treated with the primer hexamethyldisilazane (HMDS) becomes hydrophobic and as a result enhances the attachment (wetting) of the polymer, which leads to an increased field-effect mobility.[12] We used HMDS treatments for our samples in order to check if there is any modification on the electrical measurements. In Fig. 6 we present the results of this analysis: It is observed that a HMDS treatment only slightly influences the in-plane *I-V*. Moreover, the measurements are dependent whether the substrate is dipped for 1 h in a HMDS solution or when it is kept for 1 min in a HMDS vapor. But in both cases the effect of HMDS is rather small and does not significantly change the measurements.

C. Discussion

The experimental study performed on planar devices did not unambiguously explain the large currents. Variations of the polymer, substrate, and chemical treatment had only a limited effect on the measured currents, and could not account for the large discrepancy between experiments and expected SCL currents of five to six orders of magnitude. The absence of a dependence on the polymer layer thickness suggests that the current mainly flows across one of the interfaces in the device. In that case the current distribution in the in-plane device would be similar to that of a field-effect transistor. In a FET the current flows in the semiconductor between the source and the drain along the semiconductor/insulator interface and it consequently does not depend on the semiconductor thickness. The only difference with our in-plane device would be that a FET has a third electrode, the gate, which induces mobile charges in the conducting channel when biased. In an ideal transistor the conductance of the channel switches on at zero gate voltage.[14] However, in practice, it is well known that organic FETs are far from ideal, and the switch-on voltage V_{so} is often shifted to either positive or negative gate voltages.[15–17] In Fig. 7 we present the transfer characteristic of a OC_1C_{10}-PPV-based FET measured directly after fabrication. The field-effect transistor has a highly doped n^{++}-Si gate electrode, a 200 nm thermally grown SiO_2 thin film used as gate-dielectric, and gold electrodes evaporated onto the insulator to form the source and

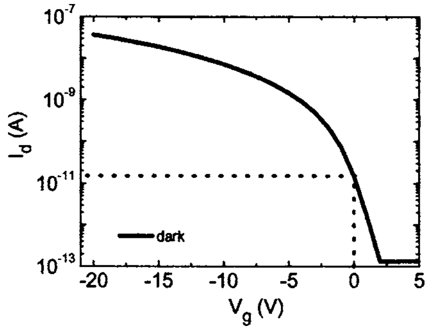

FIG. 7. Transfer characteristics of OC_1C_{10}-PPV FET measured after preparation. The polymer was spin coated in air.

drain contacts. The polymer is spin coated from toluene. The channel width W is 2500 μm, and the channel length L is 10 μm. It is observed that the FET already switches on at a positive gate voltage of $V_g=+2$ V. As a result at $V_g=0$ V the drain current is already $I_D=1.5\times10^{-11}$ A. Thus, at zero gate voltage there is already a significant number of charge carriers present in the channel that participate in the transport. It has been suggested in the literature that the observed shift of V_{so} is due to the interfacial charging at the semiconductor/insulator interface.[18,19] The origin and nature of these charges are yet to be clarified.

We now investigate the possibility that the same effect of interface charging is able to explain the large currents that we observed in the planar devices. By comparing the current of the in-plane device and the FET we can estimate the surface charge carrier density and corresponding mobility required to explain the large in-plane currents. The product of the surface charge (Q_s) and mobility μ can be determined in the in-plane device by modeling the experimental linear data with the equation $I=W/LQ_s\mu V$ (see line in Fig. 8) and amounts to 4×10^{-12} F m^2/s. We calculate now the surface charge (C_iV_g) and the field-effect mobility for each gate voltage in the FET using the equation for the field-effect current $I_d=W/L(C_iV_g)\mu V_d$, where $C_i=17\times10^{-5}$ F/m^2 and $V_d=0.1$ V. The same product of the surface charge $\times$ mobility corresponds in the FET to a gate voltage $V_g=-4$ V. The field-effect mobility that corresponds to $V_g=-4$ V is 6×10^{-9} m^2/V s. Following this analysis the enhanced current can be explained by assuming that an in plane thus behaves like an ideal FET which is biased at -4 V. Note

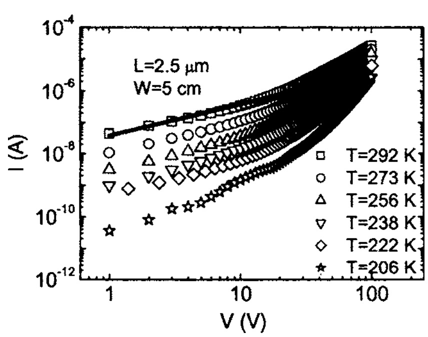

FIG. 8. Experimental *I-V* characteristics of a OC_1C_{10}-PPV in-plane diode at various temperatures.

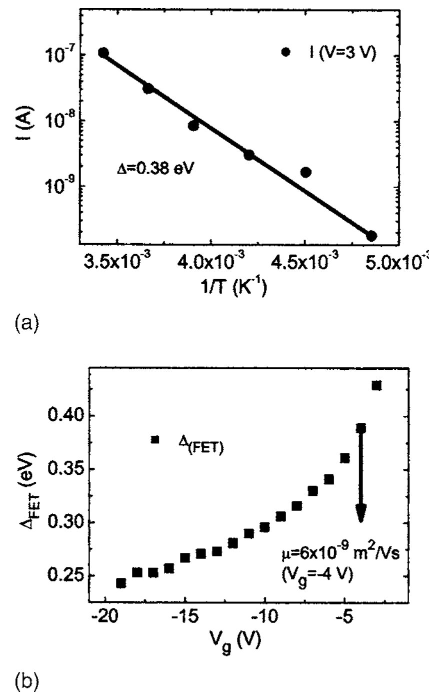

FIG. 9. The activation energy of the experimental linear current that flows in the OC_1C_{10}-PPV planar device (a) and the activation energy of the drain current that flows in the accumulation channel of the OC_1C_{10}-PPV FET (b).

that the larger mobility in the in-plane device as compared to the mobility measured in the LED structure originates from the large interfacial charge carrier density.[8]

An important way to check the presence of such a channel with enhanced charge carrier density is to compare the activation energy (Δ) of our planar device with that of a FET. In order to determine Δ we performed temperature measurements for OC_1C_{10}-PPV in both planar device and FETs. In Fig. 8 the temperature scan for a OC_1C_{10}-PPV planar device is presented in a temperature range of 292–206 K.

An activation energy $\Delta=0.39$ eV has been determined for this device [Fig. 9(a)]. From the FET measurements[8] the activation energy of $\Delta=0.39$ eV corresponds exactly to the activation energy at $V_g=-4$ V [see Fig. 9(b)]. This identical temperature dependence confirms that the in-plane device indeed acts like a FET that is switched on with a certain gate voltage. The effective gate voltage in the in-plane device might originate from the charging of the substrate/polymer interface during processing. This will be the subject of further research. The temperature dependence of the NRS-based devices showed the same consistent temperature behavior.

An important question is now whether the same effects also play a role in earlier reported measurements on in-plane devices.[5–7] In the case of PPV films[5] currents of up to 1×10^{-8} A for $V=500$ V have been measured in a Au–PPV–Au structure with $W=600$ μm and $L=30$ μm. These currents are typically 10^4 higher than what is expected from the SCL current. Apparently, also in these devices interface charges have significantly enhanced the current. Furthermore, on these devices also spatially resolved electroluminescence measurements have been performed. However, the presence of a conducting channel along the surface with high carrier density will modify the electroluminescence emission region. As a result such a measurement does not reflect the intrinsic in-plane transport and luminescent properties of the polymer.

IV. CONCLUSIONS

In conclusion current-voltage measurements from PPV-based planar devices are analyzed. We showed that the current is proportional with the electric field and five to six orders of magnitude higher than the expected space-charge limited current. The current is independent of the layer thickness, showing that it is flowing along one of the interfaces. However, the current enhancement is not sensitive to the polymer or the substrate used. The treatment of the substrate with HMDS did not significantly influences the *I*-*V* measurements. Direct comparison of the planar devices with FETs revealed that the magnitude and temperature dependence of the current in the planar devices resemble the current in a FET that is biased with a gate voltage.

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